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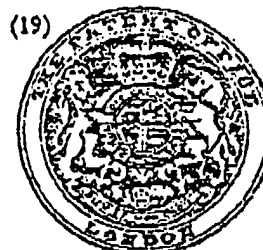
PATENT SPECIFICATION

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(19)



(54) PROCESS FOR PRODUCING GRAPHITE BODIES

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of LEONARD SIDNEY SINGER and IRWIN CHARLES LEWIS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a graphite body, such as a graphite electrode, having a very low longitudinal coefficient of thermal expansion.

Graphite shapes having low coefficients of thermal expansion, such as graphite electrodes, are generally prepared by admixing an oriented coke with a thermoplastic carbonizing binder, such as a coal tar pitch or a petroleum pitch, extruding or molding the resulting mixture into a desired shape, and then carbonizing and graphitizing the shaped article to produce a graphite body. The oriented coke employed in such process is ordinarily produced by the carbonization of a selected feedstock in a delayed coker. Although the shaped graphite articles produced in this manner have low coefficients of thermal expansion, means for further reducing the coefficients of thermal expansion of such graphite articles have been constantly sought so as to improve the performance of these articles in the high temperature surroundings in which they are employed.

Graphite shapes can also be produced as described by Grindstaff et al. in U.S. patent 3,787,541 by heating a hydrocarbon feed for a time sufficient to form a pitch containing at least 75 per cent mesophase, extruding the mixture into a desired shape, and then carbonizing and graphitizing the shaped body. However, both high temperatures and pressures are required to extrude large bodies by this technique, and upon graphitization such

bodies, like graphite bodies produced by conventional techniques, have higher than desired coefficients of thermal expansion.

In accordance with the present invention there is provided a process for producing a graphite body having a longitudinal coefficient of thermal expansion of less than $0.1 \times 10^{-6}/^{\circ}\text{C}$. which comprises extruding, in an oxygen-free atmosphere, a carbonaceous pitch having a mesophase content of at least 40 percent by weight into a shaped body having pitch molecules preferentially aligned along its length, said pitch being one which under quiescent conditions forms a bulk mesophase having large coalesced domains in excess of one hundred microns; heating the shaped body in an oxidizing atmosphere at a temperature sufficiently elevated and for a time sufficiently prolonged to thermoset the body to an extent which will allow it to maintain its shape upon heating to more elevated temperatures; and then further heating the thermoset body in an oxygen-free atmosphere to a temperature sufficiently elevated to produce a highly oriented coke; admixing said oriented coke which has an aspect ratio of at least 2:1 with a thermoplastic carbonizable binder so as to form a mixture containing from 50 per cent by weight to 80 per cent by weight of said coke and from 20 per cent by weight to 50 per cent by weight binder; extruding the resulting mixture into a desired shaped article; and then carbonizing and graphitizing the shaped article to produce a graphite body.

Mesophase pitches are pitches which have been transformed, in whole or in part, to a liquid crystal or so-called "mesophase" state. Such pitches by nature contain easily oriented molecules, and when these pitches are extruded, spun, or calendered into a desired shape, the pitch molecules are preferentially aligned along the length of the shaped body (with grain or parallel to the direction of the elongation). When the shaped body is thermoset and then heated in an oxygen-free atmos-

REFERENCE

Brit. 1,526,809

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phere to a carbonizing temperature, a highly oriented coke is obtained. If this coke is then admixed with a thermoplastic carbonizable binder, and the mixture extruded into a desired shape which is in turn carbonized and graphitized, the resulting body has a longitudinal (with grain) coefficient of thermal expansion which is lower than that of like shapes prepared in the same manner from an identical binder and coke produced from the same precursor pitch by conventional delayed coking techniques. The longitudinal (with grain) coefficients of thermal expansion of such shapes at room temperature have been found to be less than $0.1 \times 10^{-4}/^{\circ}\text{C}$. and, in some instances, to have a negative value approaching the in-plane value of single crystal graphite ($-1.5 \times 10^{-4}/^{\circ}\text{C}$), e.g., as low as $-0.7 \times 10^{-4}/^{\circ}\text{C}$. Such low coefficients of thermal expansion have never been observed heretofore in fabricated graphite bodies.

When natural or synthetic pitches having an aromatic base are heated under quiescent conditions at a temperature of 350°C .— 500°C ., either at constant temperature or with gradually increasing temperature, small insoluble liquid spheres begin to appear in the pitch which gradually increase in size as heating is continued. When examined by electron diffraction and polarized light techniques, these spheres are shown to consist of layers of oriented molecules aligned in the same direction. As these spheres continue to grow in size as heating is continued, they come in contact with one another and gradually coalesce with each other to produce larger masses of aligned layers. As coalescence continues, domains of aligned molecules much larger than those of the original spheres are formed. These domains come together to form a bulk mesophase wherein the transition from one oriented domain to another sometimes occurs smoothly and continuously through gradually curving lamellae and sometimes through more sharply curving lamellae. The differences in orientation between the domains create a complex array of polarized light extinction contours in the bulk mesophase corresponding to various types of linear discontinuity in molecular alignment. The ultimate size of the oriented domains produced is dependent upon the viscosity, and the rate of increase of the viscosity, of the mesophase from which they are formed, which, in turn are dependent upon the particular pitch and the heating rate. In certain pitches, domains having sizes in excess of one hundred microns and as large as several thousand microns are produced. In other pitches, the viscosity of the mesophase is such that only limited coalescence and structural rearrangement of layers occur, so that the ultimate domain size does not exceed one hundred microns.

The highly oriented, optically anisotropic, insoluble material produced by treating pitches

in this manner has been given the term "mesophase", and pitches containing such material are known as "mesophase pitches". Such pitches, when heated above their softening points, are mixtures of two immiscible liquids, one the optically anisotropic, oriented mesophase portion, and the other the isotropic non-mesophase portion. The term "mesophase" is derived from the Greek "mesos" or "intermediate" and indicates the pseudocrystalline nature of this highly-oriented, optically anisotropic material.

Carbonaceous pitches having a mesophase content of at least 40 per cent by weight are suitable for processing into shaped oriented bodies which can be thermoset and carbonized to produce highly oriented coke suitable for use in the present invention. In order to obtain the desired product from such pitch, however, the mesophase contained therein must, under quiescent conditions, form a bulk mesophase having large coalesced domains, i.e., domains of aligned molecules in excess of one hundred microns. Pitches which form stringy bulk mesophase under quiescent conditions, having small oriented domains, rather than large coalesced domains, are unsuitable. Such pitches form mesophase having a high viscosity which undergoes only limited coalescence, insufficient to produce large coalesced domains having sizes in excess of one hundred microns. Instead, small oriented domains of mesophase agglomerate to produce clumps or stringy masses wherein the ultimate domain size does not exceed one hundred microns. Certain pitches which polymerize very rapidly are of this type.

Carbonaceous pitches having a mesophase content of at least 40 per cent by weight can be produced in accordance with known techniques by heating a carbonaceous pitch in an inert atmosphere at a temperature above 350°C . for a time sufficient to produce the desired quantity of mesophase. By an inert atmosphere is meant an atmosphere which does not react with the pitch under the heating conditions employed, such as nitrogen, argon, xenon or helium. The heating period required to produce the desired mesophase content varies with the particular pitch and temperature employed, with longer heating periods required at lower temperatures than at higher temperatures. At 350°C ., the minimum temperature generally required to produce mesophase, at least one week of heating is usually necessary to produce a mesophase content of about 40 per cent. At temperatures of from 400°C . to 450°C ., conversion to mesophase proceeds more rapidly, and a 50 per cent mesophase content can usually be produced at such temperatures within about 1—40 hours. Such temperatures are preferred for this reason. Temperatures above 500°C . are undesirable, and heating at this temperature should not be employed for more than about 5 minutes to

avoid conversion of the pitch to coke.

The degree to which the pitch has been converted to mesophase can readily be determined by polarized light microscopy and solubility examinations. Except for certain non-mesophase insolubles present in the original pitch or which, in some instances, develop on heating, the non-mesophase portion of the pitch is readily soluble in organic solvents such as quinoline and pyridine, while the mesophase portion is essentially insoluble.⁽¹⁾ In the case of pitches which do not develop non-mesophase insolubles when heated, the insoluble content of the heat treated pitch over and above the insoluble content of the pitch before it has been heat treated corresponds essentially to the mesophase content.⁽²⁾ In the case of pitches which do develop non-mesophase insolubles when heated, the insoluble content of the heat-treated pitch over and above the insoluble content of the pitch before it has been heat treated is not solely due to the conversion of the pitch to mesophase, but also represents non-mesophase insolubies which are produced along with the mesophase during the heat treatment. The presence or absence of mesophase can be visually observed by polarized light microscopy examination of the pitch (see, e.g., Brooks, J. D., and Taylor, G. H., "The Formation of Some Graphitizing Carbons," *Chemistry and Physics of Carbon*, Vol. 4, Marcel Dekker, Inc., New York, 1968, pp. 243—268; and Dubois, J., Agache, C., and White, J. L., "The Carbonaceous Mesophase Formed in the Pyrolysis of Graphitizable Organic Materials", *Metallography* 3, pp. 337—369, 1970). The amounts of such mesophase may also be visually estimated in this manner.

Aromatic base carbonaceous pitches having a carbon content of from 92 per cent by weight to 96 per cent by weight and a hydrogen content of from 4 per cent by weight to 8 per cent by weight are generally suitable for producing mesophase pitches which can be employed to produce the highly oriented bodies suitable for use in the present invention. Petroleum pitch and coal tar pitch are preferred starting materials. Petroleum pitch can be derived from the thermal or catalytic cracking of petroleum fractions. Coal tar pitch is similarly obtained by the destructive distillation of coal. Some pitches, such as fluoranthene pitch, poly-

merize very rapidly when heated and fail to develop large coalesced domains of mesophase, and are, therefore, not suitable precursor materials.

After the desired mesophase pitch has been prepared, it is continuously processed into a shaped body using the conventional techniques of extrusion, spinning, or calendering. In order to prevent oxidation of the pitch, it should be shaped in an oxygen-free atmosphere, such as the inert atmospheres described above. Rods, bars, filaments, and sheets of oriented pitch having a diameter or thickness of up to about one mm., or more, can be conveniently prepared in this manner. As noted above, however, in order to obtain oriented bodies which can be thermoset and carbonized to produce highly oriented coke, the pitch employed must, under quiescent conditions, form a bulk mesophase having large coalesced domains.

The temperature at which the pitch is shaped depends, of course, upon the temperature at which the pitch exhibits a suitable viscosity, and at which the higher-melting mesophase portion of the pitch can be easily deformed and oriented. Since the softening temperature of the pitch, and its viscosity at a given temperature, increases as the mesophase content of the pitch increases, the mesophase content should not be permitted to rise to a point which raises the softening point of the pitch to excessive levels. For this reason, pitches having a mesophase content of more than 90 per cent are generally not employed. Pitches having a mesophase content of from 40 per cent by weight to 90 per cent by weight, can be readily shaped at temperatures at which they exhibit a viscosity of from 10 poises to 10,000 poises, usually at from 310°C. to 450°C. Viscosities of from 10 poises to 200 poises are suitable for fiber spinning. When extrusion techniques are employed, the pitch should have a viscosity of from 100 poises to 1000 poises, while viscosities in the range of from 200 poises to 10,000 poises are suitable for calendering of the pitch.

The shaped bodies produced in this manner are highly oriented materials having a high degree of preferred orientation of their molecules parallel to the direction of the elongation (with grain), as shown by their X-ray diffraction patterns. This preferred orientation is apparent from the short arcs which constitute the (002) band of the diffraction patterns. Microdensitometer scanning of the (002) bands of the exposed X-ray film indicate this preferred orientation to be generally from 20° to 35°, usually from 25° to 30° (expressed as the full

⁽¹⁾ The percent of quinoline insolubles (Q.I.) of a given pitch is determined by quinoline extraction at 75°C. The per cent of pyridine insolubles (P.I.) is determined by Soxhlet

" The insoluble content of the untreated pitch is generally less than 1 per cent (except for certain coal tar pitches) and consists largely of coke and carbon black found in the original pitch.

intensity distribution).

The shaped body produced in this manner is then heated in an oxidizing atmosphere for a time sufficient to thermoset the body to an extent which will allow the body to maintain its shape upon heating to more elevated tem-

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peratures. The oxidizing atmosphere may be pure oxygen, nitric oxide, or any other appropriate oxidizing atmosphere. Most conveniently, air is employed as the oxidizing atmosphere.

The time required to thermoset the shaped bodies of the invention will, of course, vary with such factors as the particular oxidizing atmosphere, the temperature employed, the dimensions of the bodies, the particular pitch from which the bodies are shaped, and the mesophase content of such pitch. Generally, however, thermosetting of such bodies can be effected in relatively short periods of time, usually in from 5 minutes to 120 minutes.

The temperature employed to effect thermosetting of these bodies must, of course, not exceed their softening temperatures. The maximum temperature which can be employed will thus depend upon the particular pitch from which the bodies were shaped, and the mesophase content of such pitch. The higher the mesophase content of the body, the higher will be its softening temperature, and the higher the temperature which can be employed to effect thermosetting. At higher temperatures, of course, thermosetting can be effected in less time than is possible at lower temperatures. Bodies having lower mesophase content, on the other hand, require relatively longer heat treatment at somewhat lower temperatures.

A minimum temperature of at least 250°C. is generally necessary to effectively thermoset the shaped bodies produced in accordance with the invention. Temperatures in excess of 400°C. may cause melting and/or excessive burn-off of the bodies and should be avoided. Preferably, temperatures of from 275°C. to 390°C. are employed. At such temperatures, the required amount of thermosetting can usually be effected within from 5 minutes to 120 minutes.

After the shaped body of the invention has been thermoset as required, it is further heated to a carbonizing temperature. At a temperature of about 1000°C., bodies having a carbon content greater than 98 per cent by weight are obtained. At temperatures in excess of 1500°C., these bodies are essentially completely carbonized. Such heating should be conducted in an oxygen-free atmosphere, such as the inert atmospheres described above, to prevent further oxidation of the body. Because these bodies have been infusibilized, they are capable of being carbonized free of support.

In order to ensure that the expulsion of volatiles from the bodies during carbonization does not occur so rapidly as to disrupt the structures thereof, the heating rate must be controlled so that the volatilization does not proceed at an excessive rate. Particular care must be taken in heating the bodies to a temperature of about 500°C. While very thin bodies, e.g., fibers or sheets of from about 8—15 microns in diameter or thickness, can

be heated to about 500°C. fairly rapidly, e.g. in about 5 minutes, larger bodies of about 1 mm. diameter or thickness require longer heating schedules, e.g., from 8 hours to 20 hours. After the initial expulsion of volatiles up to about 500°C. has been completed, the bodies may be heated to their final carbonizing temperature, usually in the range of from 900°C to 1500°C., and usually within from 5 minutes to 10 hours.

The coke bodies produced in this manner have a highly oriented structure characterized by the presence of carbon crystallites preferentially aligned along the lengths of the bodies (with grain parallel to the direction of elongation), as shown by the short arcs which constitute the (002) band of their X-ray diffraction patterns. Microdensitometer scanning of the (002) band of the exposed X-ray film indicates the preferred orientation parameter (FWHM) of coke carbonized to about 1000°C. to be less than 45°, usually from 30° to 40°. Coke carbonized to about 1500°C. has a higher degree of preferred orientation, i.e., a preferred orientation parameter (FWHM) of from 20° to 30°. Further improvement in the degree of preferred orientation is obtained by heating the coke at still higher temperatures. If desired, such coke may be heated, as described hereinbefore, to a graphitizing temperature in a range of from 2500°C. to 3300°C.

The oriented coke produced in this manner is then admixed with a thermoplastic carbonizable binder to form a mixture which is then extruded into a desired shape which is in turn carbonized and graphitized, in accordance with conventional techniques. The coke may be crushed or sized to facilitate admixture with the carbonizable binder; however, care should be taken to maintain the aspect ratio of the coke at at least 2:1 (by aspect ratio of the coke is meant the ratio of the width grain dimension to the against grain dimension). The graphitized shapes prepared in this manner have been found to have longitudinal (with grain) coefficients of thermal expansion which are lower than those of like shapes prepared in the same manner from an identical binder and coke produced from the same precursor pitch by conventional delayed coking techniques. Typically, the longitudinal (with grain) coefficients of thermal expansion of such shapes at room temperature have been found to be less than $0.1 \times 10^{-6}/^{\circ}\text{C}$, and, in some instances, to have a negative value approaching the in-plane value of single crystal graphite, e.g., as low as $-0.7 \times 10^{-6}/^{\circ}\text{C}$. Conventional graphite shapes typically have longitudinal (with grain) coefficients of thermal expansion of between $0.5 \times 10^{-6}/^{\circ}\text{C}$. and $1.0 \times 10^{-6}/^{\circ}\text{C}$.

The crushed or sized coke should be admixed with a thermoplastic carbonizable aromatic binder, such as coal tar pitch or petroleum pitch, in an amount sufficient to form a

5 mixture containing from 50 per cent by weight
to 80 per cent by weight coke and from 20
per cent by weight to 50 per cent by weight
binder. Preferably, such mixture contains from
10 55 per cent by weight to 75 per cent by weight
coke and from 25 per cent by weight to 45
per cent by weight binder. After a substan-
tially homogeneous mixture has been obtained,
the mixture is extruded into a desired shape by
15 means of an auger extruder or other conven-
tional technique. Temperatures of from 100°C.
to 200°C., preferably from 110°C. to 150°C.,
are generally employed, depending, of course,
upon the temperature at which the mixture
exhibits a suitable viscosity.

Carbonization of the shaped article may be
effected by heating the article in a substantially
oxygen-free atmosphere to a temperature suf-
ficiently elevated to expel volatiles and reduce
20 the binder to a carbon residue which perma-
nently binds the aggregate body. A carboniza-
tion temperature of about 1600°C. is generally
effective to drive off most of the volatile mat-
ter and produce a body having a carbon content
greater than 98 per cent by weight, and at
25 temperatures in excess of 1500°C., and body
is essentially completely carbonized. The article
should be heated gradually, of course, so as to
expel the volatiles at a rate which will not rup-
30 ture the structure. The time required to effect
carbonization without rupturing the structure
will, of course, depend upon the tempera-
ture and thickness of the article, with periods
of from 10 hours to 300 hours being sufficient
35 for most structures. A graphitized body is pro-
duced by further heating at temperatures of
from 2500°C. to 3300°C., preferably from
2800°C. to 3000°C. Residence times of from
1 minute to 240 minutes are usually sufficient.
40 The following examples are set forth for
purposes of illustration so that those skilled in
the art may better understand the invention.
It should be understood that they are exem-
plary only, and should not be construed as
45 limiting the invention in any manner. All co-
efficient of thermal expansion values set forth
in the examples and throughout the specifica-
tion are room temperature values.

EXAMPLE 1.

50 A commercial petroleum pitch was employed
to produce a pitch having a mesophase content
of about 57 per cent by weight. The precursor
pitch had a density of 1.24 g./cc., a softening
temperature of 120°C., and contained 0.5 per
55 cent by weight quinoline insolubles (Q.I. was
determined by quinoline extraction at 75°C.).
Chemical analysis showed a carbon content of
93.3%, a hydrogen content of 5.63%, a sulfur
content of 1.0% and 0.15% ash.

60 The mesophase pitch formed coalesced
mesophase domains under quiescent conditions
and was produced by heating the precursor
petroleum pitch at a temperature of about
400°C. for about 15 hours under a nitrogen

atmosphere. After heating, the pitch contained
57 per cent by weight pyridine insolubles, in-
dicating that the pitch had a mesophase content
of close to 57 per cent (P.I. was determined
by Soxhlet extraction in boiling pyridine).

A portion of this pitch was spun continuously
into fiber about 15 microns in diameter at a
temperature of 390°C. under a nitrogen atmos-
phere. Part of this fiber was then heated in an
air-draft furnace to a temperature of 275°C.
over a period of about one hour, where the
75 temperature was maintained for about one more
hour so as to thermoset the fiber. About 300
grams of the thermoset fiber was then cut into
one-inch lengths which were placed in Pyrex
(R.T.M.) beaker and heated in a sagger to a
80 temperature of 500°C. at a rate of 60°C. per
hour, held at this temperature for 3 hours, and
then cooled to room temperature. The fibers
were then removed from the beaker and re-
heated in a graphite crucible to a temperature
85 of 1000°C. at a rate of 60°C. per hour, where
the temperature was maintained for 5 more
hours. Oxygen was excluded during heating
of the fibers to 500°C and 1000°C.

The fibers calcined in this manner were then
milled to produce a flour consisting of par-
ticles with lengths up to about 200 microns.
The milled flour was blended with a 110°C.
softening point coal tar pitch in a ratio of 100
parts by weight of flour to 80 parts by weight
95 of pitch (55 per cent by weight flour and 45
per cent by weight binder). The resulting mix-
ture was then placed in an auger extruder, the
chamber of the extruder was evacuated, and
the mixture was extruded into a rod 2 centi-
meters in diameter at a temperature of about
100 120°C. employing an extrusion pressure of
between 100 psi. and 200 psi.

The extruded rod was then heated in a
sagger to a temperature of 1000°C. at a rate
of 60°C. per hour and held at this temperature
for 2 hours, and then further heated to a tem-
perature of 3000°C. over a period of about
1 hour, and maintained at that temperature for
2 hours.

The rod produced in this manner was found
to have a longitudinal (with grain) coefficient
of thermal expansion of $-0.67 \times 10^{-6}/^{\circ}\text{C}$.
Evaluations were made from samples having
115 dimensions of 1 cm. \times 2 cm. \times 12.7 cm., which
had been cut with the grain of the rod.

On the other hand, a rod produced from
the same binder pitch and coke produced from
the same precursor pitch as the coke pro-
duced from the same precursor pitch as the
120 coke produced in accordance with the above
description, but in a conventional manner,
was found to have a longitudinal (with grain)
coefficient of thermal expansion of $0.67 \times$
10⁻⁶/°C.

EXAMPLE 2.

A portion of the mesophase pitch described
in Example 1 was extruded continuously

through a spinnerette containing 128 4-mil diameter holes at a temperature of about 370°C., under a nitrogen atmosphere, to produce filaments 50 to 85 microns in diameter. Part of these filaments were spread into a thin layer and passed through an air-draft furnace set at 380°C. The residence time of the filaments in the furnace was about 5 minutes. About 300 grams of the thermoset filaments having lengths of from about 1—5 mms. was placed in a Pyrex beaker and heated in a sagger to exclude oxygen to a temperature of 500°C. at a rate of 60°C. per hour, held at this temperature for 3 hours, and then cooled to room temperature. The filaments were then removed from the beaker and reheated, oxygen again being excluded, in a graphite crucible to a temperature of 1000°C. at a rate of 60°C. per hour, where the temperature was maintained for 5 more hours.

The filaments calcined in this manner were then blended with a 110°C. softening point coal tar pitch in a ratio of 100 parts by weight of filaments to 51 parts by weight of pitch (66 per cent by weight filaments and 34 per cent by weight binder). The resulting mixture was then placed in an auger extruder, the chamber of the extruder was evacuated, and the mixture was extruded into a rod 2 centimeters in diameter at a temperature of about 120°C. employing an extrusion pressure of about 340 psi.

The extruded rod was then heated in a sagger to a temperature of 1000°C. at a rate of 60°C. per hour and held at this temperature for 2 hours, and then further heated to a temperature of 3000°C. over a period of about 1 hour, and maintained at that temperature for 2 hours.

The rod produced in this manner was found to have a longitudinal (with grain) coefficient of thermal expansion of $-0.14 \times 10^{-4}/^{\circ}\text{C}$. Evaluations were made from samples having dimensions of 1 cm. \times 2 cm. \times 12.7 cm., which had been cut with the grain of the rod.

On the other hand, a rod produced from the same binder pitch and coke produced from the same precursor pitch as the coke produced in accordance with the above description, but in a conventional manner, was found to have a longitudinal (with grain) coefficient of thermal expansion of $0.67 \times 10^{-4}/^{\circ}\text{C}$.

EXAMPLE 3.

A commercial coal tar pitch was employed to produce a pitch having a mesophase content of about 55 per cent by weight. The precursor pitch had a density of 1.28 g./cc., a softening temperature of 113°C., and contained 0.7 per cent by weight quinoline insolubles (Q.I. was determined by quinoline extraction at 75°C.). Chemical analysis showed a carbon content of 93.8%, a hydrogen content of 4.70%, a sulfur content of 0.4%, and 0.007% ash.

The mesophase pitch was produced by heat-

ing the precursor coal tar pitch at a temperature of about 400°C. for about 18 hours under a nitrogen atmosphere. After heating, the pitch contained 55 per cent by weight pyridine insolubles, indicating that the pitch had a mesophase content of close to 55 per cent (P.I. was determined by Soxhlet extraction in boiling pyridine).

A portion of this pitch was spun continuously into fiber about 15 microns in diameter at a temperature of 400°C. under a nitrogen atmosphere. Part of this fiber was then heated in an air-draft furnace to a temperature of 275°C. over a period of about one hour, where the temperature was maintained for about one more hour so as to thermoset the fiber. About 300 grams of the thermoset fiber was then cut into one-inch lengths which were placed in a Pyrex beaker and heated in a sagger to exclude oxygen to a temperature of 500°C. at a rate of 60°C. per hour, held at this temperature for 3 hours, and then cooled to room temperature. The fibers were then removed from the beaker and reheated in a graphite crucible to a temperature of 1000°C. at a rate of 60°C. per hour, oxygen being excluded, where the temperature was maintained for 5 more hours.

The fiber calcined in this manner was then milled to produce a flour consisting of particles with lengths up to about 200 microns. The milled flour was blended with a 110°C. softening point coal tar pitch in a ratio of 100 parts by weight of flour to 40 parts by weight of pitch (71 per cent by weight flour and 29 per cent by weight binder). The resulting mixture was then placed in an auger extruder, the chamber of the extruder was evacuated, and the mixture was extruded into a rod 2 centimeters in diameter at a temperature of about 120°C. employing an extrusion pressure of between 440 psi. and 460 psi.

The extruded rod was then heated in a sagger to a temperature of 1000°C. at a rate of 60°C. per hour and held at this temperature for 2 hours, and then further heated to a temperature of 3000°C. over a period of about 1 hour, and maintained at that temperature for 2 hours.

The rod produced in this manner was found to have a longitudinal (with grain) coefficient of thermal expansion of $0.06 \times 10^{-4}/^{\circ}\text{C}$. Evaluations were made from samples having dimensions of 1 cm. \times 2 cm. \times 12.7 cm., which had been cut with the grain of the rod.

On the other hand, a rod produced from the same binder pitch and coke produced from the same precursor pitch as the coke produced in accordance with the above description, but in a conventional manner, was found to have a longitudinal (with grain) coefficient of thermal expansion of $0.52 \times 10^{-4}/^{\circ}\text{C}$.

Reference is hereby made under section 9 of the Patents Act 1949 to U.K. Patent No. 1,265,552 which describes and claims a process for the production of shaped carbon

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1,526,809.

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articles which comprises the following steps:—

- a) melt spinning a pitch-like substance to form fibres,
- 5 b) rendering the said fibres infusible by heating them, the heating being carried out, at least initially in an oxidising atmosphere,
- c) mixing the infusible pitch fibres with a carbonisable binder,
- 10 d) shaping the mixture to produce an article of the desired shape, and
- e) heating the shaped article to carbonise the article.

WHAT WE CLAIM IS:—

- 15 1. A process for producing a graphite body having a longitudinal coefficient of thermal expansion of less than $0.1 \times 10^{-6}/^{\circ}\text{C.}$ which comprises extruding, in an oxygen-free atmosphere, a carbonaceous pitch having a mesophase content of at least 40 per cent by weight
- 20 into a shaped body having pitch molecules preferentially aligned along its length, said pitch being one which under quiescent conditions forms a bulk mesophase having large coalesced domains in excess of one hundred microns;
- 25 heating the shaped body in an oxidizing atmosphere at a temperature sufficiently elevated and for a time sufficiently prolonged to thermoset the body to an extent which will allow it to maintain its shape upon heating to
- 30 more elevated temperatures; and then further

heating the thermoset body in an oxygen-free atmosphere to a temperature sufficiently elevated to produce a highly oriented coke; admixing said oriented coke which has an aspect ratio of at least 2:1 with a thermoplastics carbonizable binder so as to form a mixture containing from 50 per cent by weight to 80 per cent by weight of said coke and from 20 per cent by weight to 50 per cent by weight binder; extruding the resulting mixture into a desired shaped article; and then carbonizing and graphitizing the shaped article to produce a graphite body.

2. A process as in claim 1 wherein the oxidizing atmosphere employed to thermoset the shaped body is air.

3. A process for producing graphite bodies, as claimed in claim 1 and substantially as hereinbefore described according to Example I or Example II or Example III.

4. A process as claimed in claim 1 and substantially as hereinbefore particularly described.

5. A graphite body when produced according to a process as claimed in any of claims 1 to 4.

W. P. THOMPSON & CO.,
Coopers Buildings,
12, Church Street, Liverpool, L1 3AB.
Chartered Patent Agents

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